

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
20 February 2003 (20.02.2003)

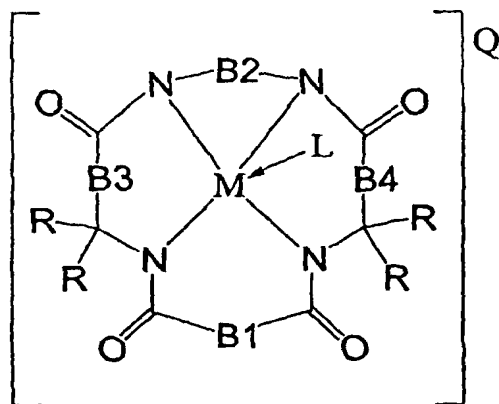
PCT

(10) International Publication Number  
WO 03/014280 A1

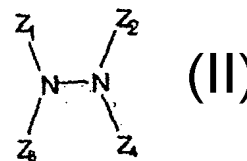
- (51) International Patent Classification<sup>7</sup>: C11D 3/39, 3/32, 3/34
- (21) International Application Number: PCT/EP02/08538
- (22) International Filing Date: 30 July 2002 (30.07.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
0118934.9 2 August 2001 (02.08.2001) GB
- (71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, MZ, OM, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).
- (71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).
- (71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).
- (72) Inventor; and  
(75) Inventor/Applicant (for US only): **OAKES, John** [GB/GB]; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).
- (74) Agents: **ELLIOTT, Peter, William** et al.; Unilever PLC, Patent Departement, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: BLEACHING COMPOSITIONS



(I)



(II)

(57) Abstract: Bleaching compositions which can be used in laundry processes comprising a metal-complexed ligand which preferably has the structure (I) wherein: B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> and B<sub>4</sub> each represent a bridging group, M is a transition metal ion, L is an axial ligand, and Q is an alkali metal counter-ion. The compositions also comprise one or more enhancer compounds for the said metal complexing ligand, said enhancer compound being preferably of the general formula (II) wherein Z<sub>1</sub>-Z<sub>2</sub> are electron-withdrawing groups, and Z<sub>3</sub> and Z<sub>4</sub> are hydrogen, or are absent when the bonding between Z<sub>1</sub> or Z<sub>2</sub> and the adjacent nitrogen in the general form is a pi-bond. The composition comprises optional surfactant, peroxygen source and builder.

WO 03/014280 A1



European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

**Published:**

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

- 1 -

## BLEACHING COMPOSITIONS

**Field of the Invention:**

5 The present invention relates to the use of certain macrocyclic metal-ligand complexes as catalytic bleaching agents. The invention will be particularly described with reference to bleaching in the context of fabric washing and  
10 laundry, although other and broader aspects of the invention are not intended to be excluded.

**Background of the Invention:**

15 It is well known that enzymes can engage in catalytic oxidation reactions. It is also known that certain compounds can facilitate the progress of these reactions. WO-A-94/12619, WO-A-94/12620 and WO-A-94/12621 (Novo  
20 Nordisk) disclose the use of simple substituted phenols, benzidine derivatives, phenothiazine derivatives and azino compounds as 'enhancers' for peroxidases and/or laccases. WO-A-97/06244 (Ciba) also discloses various enhancers, such as substituted naphthols, barbituric acids, and substituted  
25 coumarins.

Oxidation catalysts comprising non-enzyme (i.e. non-peptide) metal-complexes are also known. Such catalysts have been used in laundry compositions as components of a bleaching  
30 system. They have also been used in other chemical processes such as in the pulp and paper industry and in the cleaning of hard surfaces.

- 2 -

These catalysts generally activate  $H_2O_2$  or other peroxygen sources in water, and are effective at neutral to basic pH. Some of these catalysts are even effective with oxygen itself as the source of oxidising equivalents.

5

A specific bleaching catalyst is disclosed in WO 98/03263, filed 21 July 1997, (Collins). This comprises a macrocyclic (tetra) amido N-donor. The macrocycle is capable of complexing with a metal ion, for example an iron III or IV.

10 United States Patent 5,853,428, filed 24 Feb 1997, (Collins) discloses use of similar catalysts in laundry detergent compositions.

Although they have other uses, non-enzyme bleaching  
15 catalysts are of particular utility in the prevention of so-called 'dye transfer' in a laundry process. This occurs when dyestuffs are released from one region of a cloth article during laundering and are later re-adsorbed at another location or on another article. It is advantageous  
20 to bleach the dyestuff while it is in aqueous solution, thereby preventing or reducing its transfer.

While the present invention is described herein with specific reference to laundry processes other uses of the  
25 materials disclosed herein are not intended to be excluded. Thus the word 'dyestuff' should be interpreted in the general sense of a material giving an unwanted colour.

- 3 -

**Summary of the Invention:**

5 We have now determined that the bleaching activity of the metal-ligand catalysts may be improved by the presence of enhancers.

Accordingly, a first aspect of the present invention  
10 provides a composition comprising:

a) a non-enzyme, metal-complexing ligand which is capable,  
in its complexed form and in the presence of a source of  
oxidising equivalents of oxidising dyestuffs and/or  
15 chromophoric soils, and,

b) one or more enhancer compounds.

20 Typically, compositions according to the present invention will comprise a ligand which is pre-complexed with a metal. While in some circumstances the conditions of use may be such that the environment is rich enough in a suitable metal, and the complex may form with sufficient ease to  
25 allow for metal-ligand formation in situ, it is preferable to provide the complex ab-initio.

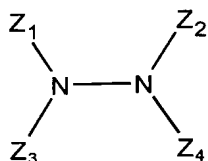
Without wishing to be limited by any theory of operation, it is believed that the metal-ligand complex can form an  
30 activated species in the presence of oxidising equivalents. This activated species then interacts with the enhancer to form an activated species of enhancer. This activated

- 4 -

species of enhancer can then interact with a dyestuff or another coloured material and bring about discolouration of that material.

- 5 Preferably the enhancers are nitrogen-containing organic molecules. More preferably, the enhancer compounds are of the general formula one, shown below:

10 General Formula One:



- 15 wherein Z<sub>1</sub>-Z<sub>2</sub> are electron-withdrawing groups, independently selected from the group consisting of optionally substituted alkyl/(hetero) (poly)aryl-, -sulfone, -sulfoxide, -sulfonate, -carbonyl, -oxalyl, -amidoxalyl, -hydrazidoxalyl, -carboxyl and esters and salts thereof, -amidyl, -  
20 hydrazidyl, and nitrile.

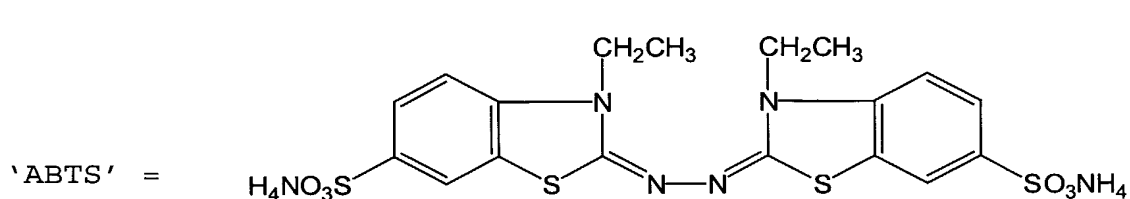
Z<sub>3</sub> and Z<sub>4</sub> are hydrogen, or are absent when the bonding between Z<sub>1</sub> or Z<sub>2</sub> and the adjacent nitrogen in the general form is a pi-bond.

25

In preferred enhancers Z<sub>3</sub> and Z<sub>4</sub> are both hydrogen (thereby forming a hydrazino compound), or Z<sub>3</sub> and Z<sub>4</sub> are both absent (thereby forming an azino compound).

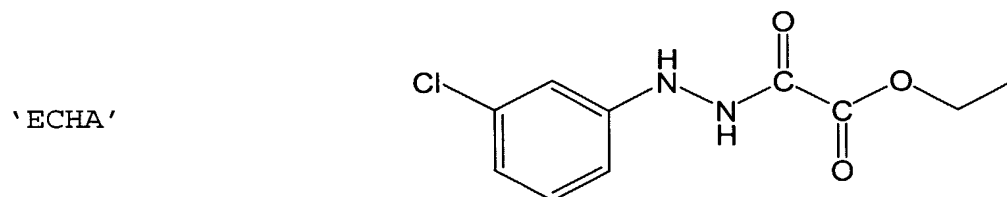
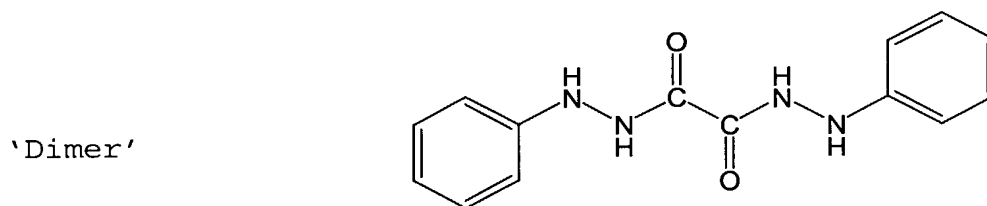
- 5 -

Particularly preferred azino enhancers are molecules of the general formula given below:



This molecule is known as 2,2'-Azino-bis(3-ethylbenzthiazoline-6-sulphonate) diammonium salt. Its CA registry number is 30931-67-0.

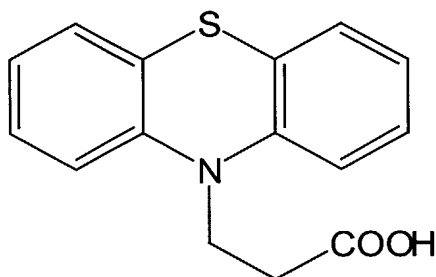
15 Preferred hydrazino enhancers may contain one or more than one of the hydrazino structures. The general formulae of two particularly preferred enhancers are given below:



- 6 -

The structure of a further enhancer, which does not have the characteristic azino- or hydrazino- bond of the preferred embodiments discussed above is given below:

5



This is phenothiazine-10-propionate (PTP), as described in  
10 US-A-5 451 337 and US-A-5 445 755.

It is believed that there are several factors which contribute to the efficacy of the compositions disclosed herein. It is believed that the activated enhancer is a  
15 relatively long-lived species, that its low molecular weight (as compared with the metal-ligand complex) promotes diffusion of the activated enhancer and that it will be effective in heterogeneous environments. It is also believed that the activated enhancer is effective at low pH's.

20

The bleach catalyst per se may be selected from a wide range of transition metal complexes of organic molecules. Suitable organic molecules (ligands) for forming complexes and complexes thereof are found, for example in: GB  
25 9906474.3; GB 9907714.1; GB 98309168.7, GB 98309169.5;



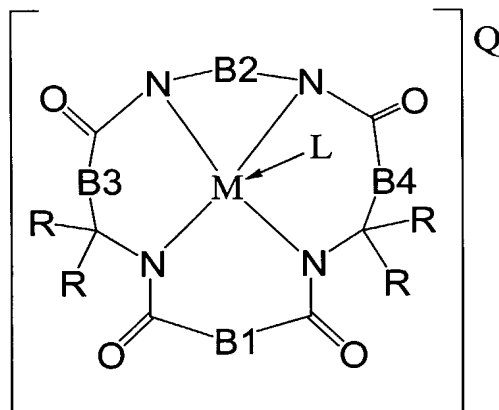
- 7 -

GB 9027415.0 and GB 9907713.3; DE 19755493; EP 999050;  
 WO-A-9534628; EP-A-458379; EP 0909809; United States Patent  
 4,728,455; WO-A-98/39098; WO-A-98/39406, WO 9748787,  
 WO 0029537; WO 0052124, and WO0060045 the complexes and  
 5 organic molecule (ligand) precursors of which are herein  
 incorporated by reference.

Preferred metal-complexed ligands are those having the  
 structure as shown in general formula 2

10

General formula 2:



Wherein:

- 15 - B<sub>1</sub>, B<sub>3</sub> and B<sub>4</sub> each represent a bridging group having  
 zero, one two or three carbon containing nodes for  
 substitution, and B<sub>2</sub> represents a bridging group having  
 at least one carbon containing node for substitution,  
 each said node containing a C(R), C(R<sub>1</sub>)(R<sub>2</sub>) or C(R)<sub>2</sub> ,

20

- 8 -

- each R substituent is the same is the same or different from the remaining R substituents, and

(i) is selected from the group consisting of alkyl,  
5 alkenyl, cycloalkyl, cycloalkenyl, aryl, alkynyl,  
alkylaryl, halogen, alkoxy, phenoxy and  
combinations thereof, or

(ii) form a substituted or unsubstituted benzene ring  
10 of which two carbons on the ring form nodes in the  
B-unit;

- M is a transition metal ion;

15 - L is an axial ligand; and,

- Q is an alkali metal or tetra-alkyl ammonium or tetra-phenyl phosphonium counter-ion.

20 Preferably, the axial ligand is selected from the group consisting of water and halide. Particularly preferred axial ligands are water and chloride.

It is within the scope of the present invention to have a  
25 bleach activator, wherein M is selected from the group consisting of Fe, Mn, Cr, Cu, Co, Ni, Mo, V, Zn and W.

These complexes are of far lower molecular weight than  
enzymes and are consequently believed to be more weight  
30 efficient as regards activation of the enhancer. However,  
the complexes tend to be expensive to synthesise and

- 9 -

consequently, their use in combination with a relatively inexpensive enhancer leads to a more cost effective system.

5 **Detailed Description of the Invention:**

Throughout the description and claims generic groups are used, for example alkyl, alkoxy, aryl etc. Unless otherwise specified the following are preferred group restrictions  
10 that may be applied to generic groups found within compounds disclosed herein:

	alkyl:	linear and branched C1-C8-alkyl, preferably C1-C6;
15	alkenyl:	C2-C8-alkenyl, preferably C3-C6;
	cycloalkyl:	C3-C8-cycloalkyl, preferably C6-C8;
	cycloalkenyl:	C4-12-cycloalkenyl (preferably C4-C8) having a single cyclic ring or multiple condensed rings and at least one point of internal 20 unsaturation which can be optionally substituted with from 1 to 3 C1-C8-alkyl groups;
	aryl:	selected from homoaromatic compounds having a molecular weight under 300, preferably 25 selected from group consisting of: phenyl; biphenyl; naphthalenyl; anthracenyl; and phenanthrenyl;
	alkynyl:	C2-C12-alkynyl; alkylaryl: C1-12-alkylaryl, wherein the aryl selected from homoaromatic 30 compounds having a molecular weight under 300;

- 10 -

halogen: selected from the group consisting of: F;  
Cl; Br and I, preferably F and Cl; and,  
alkoxy: C1-C6-alkoxy, preferably C1-C4.

5 The present invention extends to fully formulated laundry  
products containing the catalysts and enhancers disclosed  
herein. Such products will generally contain a detergent  
active and will typically contain one or more builders  
together with the typical additives used in detergent  
10 compositions.

The present invention also extends to a packaged laundry  
treatment composition comprising a bleach activator as  
defined together with an enhancer as defined, and  
15 instructions for its use.

Typically, compositions of the present invention will  
comprise a peroxygen source.

20 Further aspects of the present invention and preferred  
embodiments are described below.

**Ligands:**

25 As described above, a preferred ligand is that described  
with reference to general formula 2.

Particularly preferred ligands of general formula 2 have R =  
30 methyl. B3 and B4 are preferably absent, the two related  
sides of the ring being derived from a 'classical' amino  
acid in which the amino group is located on the alpha-

- 11 -

carbon. A preferred starting amino acid is 2-amino iso-butyrlic acid.  $(\text{H}_2\text{N}-\text{C}(\text{CH}_3)_2-\text{COOH})$ .

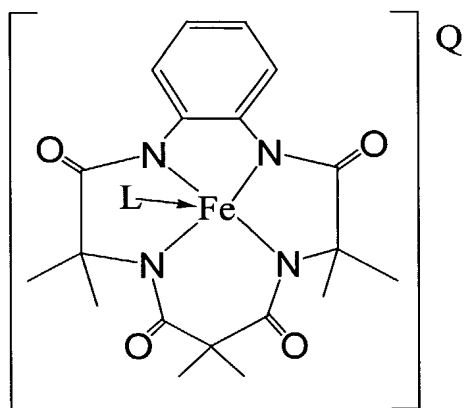
The transition metal is preferably selected from groups VI, VII, VIII, IX, X and XI of the periodic table. More preferably the metal is selected from the group consisting of Fe, Mn, Cr, Cu, Co, Ni, Mo, V, Zn and W. Particularly preferably the metal is selected from the group comprising: Fe, Mn, Cu and Co. Iron is the most preferred metal.

10

Suitable counter ions are tetra-alkyl ammonium, tetra-phenyl phosphonium, K, Li or Na, most preferably lithium.

The most preferred catalyst is that in which the ligand is 5,6-benzo-3,8,11,13-tetraoxo-2,2,9,9,12,12-hexamethyl-1,4,7,10-tetraaza-cyclo-tridecane as shown below as the Fe form, the axial ligand 'L' is water or preferably chloride. The counter-ion 'Q' is preferably lithium. The ligand is also known as 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexa-methyl-1H-1,4,8,11-benzotetraazocyclotridecane-2,5,7,10(6H,11H) tetrone.

- 12 -



The composition is preferably used in laundry wash liquor,  
 5 preferably an aqueous wash liquor.

The amount of catalyst in the composition according to the  
 present invention is sufficient to provide a concentration  
 in the wash liquor of generally 0.005  $\mu\text{M}$  to 100  $\mu\text{M}$ ,  
 10 preferably from 0.025  $\mu\text{M}$  to 50  $\mu\text{M}$ , more preferably from 0.05  
 $\mu\text{M}$  to 10  $\mu\text{M}$ .

#### Peroxygen Source:

15

While some of the catalysts described above are capable of  
 utilising atmospheric oxygen as the source of oxidising  
 equivalents, it is greatly preferred that the compositions  
 of the present invention are pre-formulated with a source of  
 20 hydroperoxyl species.

- 13 -

It is preferable that the composition contains a peroxygen bleach or a peroxy-based or -generating system. The peroxygen bleach is preferably a compound which is capable of yielding hydrogen peroxide in aqueous solution although  
5 it is possible to use more complex systems which involve peracids and/or peracid precursors.

Hydrogen peroxide sources are well known in the art. They include the inorganic peroxides, for example alkali metal  
10 peroxides, organic peroxides for example as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

15 Typical levels of peroxygen source in fully formulated composition will range from 0.05-55 wt.% with 1-40 wt.% being particularly preferred and 1-25 wt.% being most particularly preferred.

20 Typical levels of peroxygen source (as hydrogen peroxide equivalents) in fully formulated composition will be such that the in-use concentration will range from 0.005mM to 100mM with 0.025mM to 50mM being particularly preferred and 0.05mM to 10mM being most particularly preferred.

25 Preferred peroxygen sources include percarbonate and perborate.

Particularly preferred are sodium perborate tetrahydrate  
30 and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high

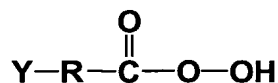
- 14 -

active oxygen content. Sodium percarbonate may also be preferred for environmental reasons.

Another suitable hydrogen peroxide generating system is a  
5 combination of a C<sub>1</sub>-C<sub>4</sub> alkanol oxidase and a C<sub>1</sub>-C<sub>4</sub> alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in WO-A-9507972, which is incorporated herein by reference.

10 Alkylhydroxy peroxides are another class of peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

Organic peroxyacids (also known as peracids) may also be  
15 suitable as components of the bleaching system. Such materials normally have the general formula:



20

wherein R is an alkyl- or alkylidene- or substituted  
alkylene group containing from 1 to about 20 carbon atoms,  
optionally having an internal amide linkage; or a phenylene  
25 or substituted phenylene group; and Y is hydrogen, halogen,  
alkyl, aryl, an imido-aromatic or non-aromatic group, a -  
COOH or -COOOH group or a quaternary ammonium group.



- 15 -

Typical monoperoxy acids useful herein include, for example:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-a-naphthoic acid;
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxy lauric acid, peroxy stearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and
- (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

- (i) 1,12-diperoxydodecanedioic acid (DPDA);
- (ii) 1,9-diperoxyazelaic acid;
- (iii) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (iv) 2-decyldiperoxybutane-1,4-dioic acid; and
- (v) 4,4'-sulphonylbisperoxybenzoic acid.

Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10 % by weight, preferably from 4-8 % by weight.

- 16 -

Peroxyacid bleach precursors are also known and amply described in literature, such as in GB-A-836988; GB-A-864,798; GB-A-907,356; GB-A-1,003,310 and GB-A-1,519,351; DE-A-3,337,921; EP-A-0,185,522; 5 EP-A-0,174,132; EP-A-0,120,591; and US-A-1,246,339; US-A-3,332,882; US-A-4,128,494; US-A-4,412,934 and US-A-4,675,393.

Another useful class of peroxyacid bleach precursors is that 10 of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US-A-4,751,015 and US-A-4,397,757, in EP-A-0,284,292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are: 2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl 15 carbonate chloride - (SPCC); N-octyl,N,N-dimethyl-N<sub>10</sub>-carbophenoxy decyl ammonium chloride - (ODC); 3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and 20 N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520; EP-A-458,396 and EP-A-464,880.

25

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors 30 including the cationic nitriles.

- 17 -

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; 2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride (SPCC); trimethyl ammonium toluoyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyl-oxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

Of the peracid precursors, TAED and SNOBS are preferred. Hydrogen peroxide based bleaching systems according to the present invention are markedly preferred to peroxyacid based systems. Where present the precursors are typically used in an amount of up to 12%, more preferably from 0.5 - 5% by weight of the composition.

#### 20 DTI Polymers:

It is advantageous for the compositions of the invention to comprise one or more dye transfer inhibition (DTI) agents. Known agents include peroxidases, phthalocyanines and polymers.

Nitrogen-containing, dye binding, DTI polymers are preferred. Of these polymers and co-polymers of cyclic amines such as vinyl pyrrolidone, and/or vinyl imidazole are preferred. Suitable polymers include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of

- 18 -

N-vinylpyrrolidone and N-vinylimidazole, and polymers of N-carboxymethyl-4-vinylpyridinium chloride.

Polyamine N-oxide polymers suitable for use herein contain  
5 units having the following structural formula:  $R-A_x-P$ ;  
wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit; A is one of the following structures: -  
NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is an  
10 aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic group or combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups, or the N-O group can be attached to both units. Preferred polyamine N-oxides are those wherein R is  
15 a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. The N-O group can be represented by the following general structures:  $N(O)(R')_{0-3}$ , or  $=N(O)(R')_{0-1}$ , wherein each R' independently represents an aliphatic, aromatic,  
20 heterocyclic or alicyclic group or combination thereof; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a  $pK_a < 10$ , preferably  $pK_a < 7$ , more preferably  $pK_a < 6$ .

25

Any polymer backbone can be used provided the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters,  
30 polyethers, polyamides, polyimides, polyacrylates and

- 19 -

mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine  
5 N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization.

10 Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferably 1,000 to 500,000; most preferably 5,000 to 100,000. This preferred class of materials is referred to herein as "PVNO". A preferred polyamine N-oxide is poly(4-vinylpyridine-N-oxide) which as  
15 an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Block or random copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (as a class, referred to as  
20 "PVP/PVI") are also preferred. Preferably the PVP/PVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000, as determined by light scattering as described in Barth, et al., Chemical Analysis, Vol. 113.

25 "Modern Methods of Polymer Characterization"). The preferred PVP/PVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or  
30 branched. Suitable PVP/PVI polymers include Sokalan<sup>(TM)</sup>

- 20 -

HP56, available commercially from BASF, Ludwigshafen, Germany.

Also preferred as dye transfer inhibition agents are  
5 polyvinylpyrrolidone polymers ("PVP") having an average  
molecular weight of from about 5,000 to about 400,000,  
preferably from about 5,000 to about 200,000, and more  
preferably from about 5,000 to about 50,000. PVP's are  
disclosed for example in EP-A-262,897 and EP-A-256,696.

10 Suitable PVP polymers include Sokalan<sup>(TM)</sup> HP50, available  
commercially from BASF. Compositions containing PVP can  
also contain polyethylene glycol ("PEG") having an average  
molecular weight from about 500 to about 100,000, preferably  
from about 1,000 to about 10,000. Preferably, the ratio of  
15 PEG to PVP on a ppm basis delivered in wash solutions is  
from about 2:1 to about 50:1, and more preferably from about  
3:1 to about 10:1.

Also suitable as dye transfer inhibiting agents are those  
20 from the class of modified polyethyleneimine polymers, as  
disclosed for example in WO-A-0005334. These modified  
polyethyleneimine polymers are water-soluble or dispersible,  
modified polyamines. Modified polyamines are further  
disclosed in US-A-4,548,744; US-A-4,597,898;  
25 US-A- 4,877,896; US-A- 4,891, 160; US-A- 4,976,879;  
US-A-5,415,807; GB-A-1,537,288; GB-A-1,498,520;  
DE-A-28 29022; and JP-A-06313271.

Preferably the bleaching composition according to the  
30 present invention comprises a dye transfer inhibition agent

- 21 -

selected from poly vinyl-pyrridine N-oxide (PVPy-NO),  
polyvinyl pyrrolidone (PVP), polyvinyl imidazole,  
N-vinylpyrrolidone and N-vinylimidazole copolymers  
(PVP/PVI), copolymers thereof, and mixtures thereof.

5

The amount of dye transfer inhibition agent in the  
composition according to the present invention will be from  
0.01 to 10 %, preferably from 0.02 to 5 %, more preferably  
from 0.03 to 2 %, by weight of the composition.

10

#### **Surfactants and Builders:**

The present invention has particular application in  
detergent bleaching, especially for laundry cleaning.  
Accordingly, the composition preferably contains a surface-  
active material, optionally together with detergency  
builder.

15

The composition may contain a surface-active material in an  
amount, for example, of from 10 to 50% by weight.

20

The surface-active material may comprise materials which are  
naturally derived, such as soap, or a synthetic material  
selected from anionic, nonionic, amphoteric, zwitterionic,  
cationic actives and mixtures thereof. Many suitable  
actives are commercially available and are fully described  
in the literature, for example in "Surface Active Agents and  
Detergents", Volumes I and II, by Schwartz, Perry and Berch.

25

30

- 22 -

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl groups containing from about 8 to about 22 carbon atoms, the term "alkyl" being used to  
5 include the alkyl portion of higher aryl groups.

Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for  
10 example, from tallow or coconut oil; sodium and ammonium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates, particularly sodium linear secondary alkyl (C<sub>10</sub>-C<sub>15</sub>) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty  
15 acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C<sub>9</sub>-C<sub>18</sub>) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and  
20 neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C<sub>8</sub>-C<sub>20</sub>) with sodium bisulphite and those derived by reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and then hydrolysing  
25 with a base to produce a random sulphonate; sodium and ammonium (C<sub>7</sub>-C<sub>12</sub>) dialkyl sulphosuccinates; and olefin sulphonates, which term is used to describe material made by reacting olefins, particularly (C<sub>10</sub>-C<sub>20</sub>) alpha-olefins, with



- 23 -

SO<sub>3</sub> and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C<sub>10</sub>-C<sub>15</sub>) alkylbenzene sulphonates (C<sub>10</sub>-C<sub>15</sub> LAS), and sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl ether sulphates (C<sub>16</sub>-C<sub>18</sub> LES).

5

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with  
10 alkyl (C<sub>6</sub>-C<sub>22</sub>) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl  
15 polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Amphoteric or zwitterionic surface-active compounds can also  
20 be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic  
25 actives.

The composition will preferably comprise from 1 to 15 % wt of anionic surfactant and from 10 to 40 % by weight of nonionic surfactant.

- 24 -

Preferred embodiments of the present invention comprise a mixed active system which comprises both anionic and nonionic surfactants. It is believed that the catalysts become less effective as the level of nonionic approaches 100% on surfactant. Conversely, where nitrogen-containing, dye binding, DTI polymers are used, the effectiveness of these polymers is reduced at high levels of anionic surfactant.

It is preferable that the level of anionic surfactant (on total surfactant) ranges from 10-90%wt and that the level of nonionic ranges from 90-10%wt (on total surfactant). It is especially preferred to use 30-60%wt/surfactant of anionic surfactant selected from: LAS, PAS, soap and mixtures thereof, together with 70-40%wt/surfactant of ethoxylated alcohol nonionic surfactant.

In absence of DTI polymer which is sensitive to surfactants, the formulation can contain 100% Anionic surfactant.

The composition may also contain a detergency builder, for example in an amount of from about 5 to 80 % by weight, preferably from about 10 to 60 % by weight.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium

- 25 -

tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed  
5 in US-A-4,144,226 and US-A-4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

10

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known  
15 as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

In particular, the composition may contain any one of the organic and inorganic builder materials, though, for  
20 environmental reasons, phosphate builders are preferably omitted or only used in very small amounts. Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy  
25 malonate, carboxymethyloxy succinate and water-insoluble crystalline or amorphous aluminosilicate builder materials, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

30

- 26 -

It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferably not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower  
5 alkaline region of up to 10.

Apart from the components already mentioned, the composition can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing  
10 detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-  
15 redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate and  
20 sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

25 When using a hydrogen peroxide source, such as sodium perborate or sodium percarbonate, as the bleaching compound, it is preferred that the composition contains not more than 5 % by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to  
30 substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

- 27 -

Of the additives, transition metal sequestrants such as EDTA and the phosphonic acid derivatives, e.g. ethylene diamine tetra-(methylene phosphonate)-EDTMP- are of special  
5 importance, as not only do they improve the stability of the catalyst/H<sub>2</sub>O<sub>2</sub> system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above.

10 Other suitable transition metal sequestrants are known and can be chosen by those skilled in the art, for example aminocarboxylates, aminophosphonates, and polyfunctionally substituted aromatic chelating agents, as disclosed further in WO-A-98/39406. If present, the sequestrants are  
15 generally present in amounts of 0.001 to 15%, more preferably 0.01 to 3.0%, by weight of the composition.

The present invention may be conveniently embodied in a solid form of product, which includes both a powder or  
20 tablet form of product. Both of these forms may be homogeneous or non-homogeneous. For example tablets may comprise a plurality of discrete regions which include some ingredients only, while powders may comprise mixed granules of differing compositions.

25  
**Examples:**

In order that the invention may be further and better understood it will be described in detail with reference to  
30 following non-limiting examples.

- 28 -

The catalyst referred to in the examples is the Fe complex of 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1H-1,4,8,11-benzotetraazocyclotri-decane -2,5,7,10 (6H,11H) tetrone, with lithium as the counter-ion and water as the axial  
5 ligand. This was synthesised in accordance with the method set out in our co-pending patent application GB 0020846.2.

The model detergent used in the examples was such that the wash liquor contained 1g/L of a 50/50 mixture of LAS and the  
10 nonionic Synperonic A7, 1g/L of sodium tripolyphosphate, 0.4 g/L sodium carbonate and 20 microlitres of sequestrant (Dequest™ 2047).

Washes were simulated in a shaker-bath or Rotawash  
15 Linitester™ at 40°C, using 30 minutes agitation in 100-200ml of wash liquor.

All fabrics were measured after washing on an ICS Texicon Spectraflash™ 500 which was calibrated using the following  
20 settings:

UV Excluded - (420nm cut-off)  
Specular included  
Large aperture

25

Each monitor was measured through one thickness of cloth with bleached, non-fluorescent mercerised white cotton sheeting as the reference standard. Each monitor was measured four times and the average of these four  
30 measurements was taken to be the value of that monitor.

- 29 -

Reflectance values were taken and converted into delta E values by a computer software package which reported average delta E values according to the following equation:

5 
$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)}$$

**Example 1: Removal of Tomato Stains:**

Four replicates of 5cm square tomato-stained cotton cloths  
10 were washed in 100ml phosphate-built detergent liquor using  
a shaker bath at 40°C.

Where present, levels of additional components are: 50µM  
Enhancer, 500µM H2O2, 1µM catalyst.

15

Data as presented in Table 1 are averages of eight readings  
(2 per side, per cloth). In this experiment, higher values  
of delta-E indicate that more of the stain has been removed  
from the cloth.

20

Table 1 shows that peroxide alone shows a very slight  
improvement over just detergent but has no significant  
effect on tomato stain, while the catalyst + H2O2 has  
significant stain removal benefits. It can be seen that, in  
25 particular, the enhancer ABTS greatly increases stain  
removal.

- 30 -

**Table 1: Delta-E Values for Tomato Stained Cloth**

	Detergent liquor Only	Detergent liquor plus peroxide	Detergent liquor plus peroxide and catalyst
Control (- enhancer)	9.1	9.2	12.6
'Dimer' (+ enhancer)	9.8	9.9	13.2
'ABTS' (+ enhancer)	8.9	9.5	24.4

5 **Example 2: Pick-up on white from Direct Green Dye:**

One 10x10cm Direct Green 26 dyed (fixed) cotton cloth and  
 one 10x10 cm white cotton monitor cloth were washed together  
 in 200ml liquor using a Rotawash (Linitester). Data values  
 10 (delta E) shown in table 2 are averages of 4 readings (2 per  
 side, per monitor cloth).

In this experiment the delta-E represents the amount of dye  
 which has been transferred from the green cloth to the white  
 15 monitor. Therefore, lower levels of delta-E are  
 representative of better results.

Where present, levels of additional components are: 100 $\mu$ M  
 ABTS, 500 $\mu$ M H<sub>2</sub>O<sub>2</sub>, 1 $\mu$ M catalyst.

20

Results in Table 2 show that peroxide alone did nothing to  
 prevent dye transfer. Addition of catalyst has an effect  
 which is further improved by the presence of the enhancer.



- 31 -

**Table 2: Delta-E values Direct Green Pick-up**

	Detergent liquor Only	Detergent liquor plus peroxide	Detergent liquor plus peroxide and catalyst
Control (- enhancer)	7.5	7.5	3.7
'ABTS' (+ enhancer)	-	-	2.3

5

**Example 3: ABTS - pH profile of tea stain bleaching:**

One 10x10cm tea stained monitor cloth (BC1 stained) was washed in 100ml detergent (1g/L 50/50 LAS/A7, 1g/L sodium sulphate) 20 $\mu$ M EDTA. This was buffered in phosphate or borax. Washes were 30 min in a shaker-bath at 40°C.

Data values (Delta R, 460nm - nil fluorescence) are given in Table 3 below, these are averages of 4 readings, two per side. Where present, examples have 100 $\mu$ M ABTS, 1000 $\mu$ M H<sub>2</sub>O<sub>2</sub>, 1 $\mu$ M catalyst. As with Example 1 above the delta-E values are higher for those experiments in which more of staining is removed from the cloth.

Table 3 shows that addition of ABTS extends the pH profile to better bleaching at low pH. In the control experiments and those with either peroxide or peroxide plus enhancer, the bleaching performance falls off with decreasing pH. When the enhancer is present, the performance does not fall off so quickly at lower pH.

- 32 -

**Table 3: pH range of catalyst/enhancer:**

Buffered pH	Control	Plus Peroxide	Plus Peroxide and catalyst	Plus peroxide, catalyst and ABTS
6.0	4.8	5.8	5.17	6.35
8.0	3.99	4.12	4.16	7.06
9.2	4.82	4.87	4.34	6.66
10.0	5.22	5.8	6.14	6.26
10.8	6.62	7.88	7.6	7.22

5

**Example 4: Bleaching on tea stains:**

Two 10x10cm BC1 cloths were washed 200ml phosphate-built detergent liquor (1g/L 50/50 LAS/A7, 1g/L STP, 0.4g/L

10 Na<sub>2</sub>CO<sub>3</sub>) containing 20 $\mu$ M Dequest, for 30 min in the Rotawash (Linitester) at 40'C. Data values shown in table 4 (Delta E) and are averages of 4 readings (2 per side, per cloth). Where present, additional components are 100 $\mu$ M ABTS, 500 $\mu$ M H<sub>2</sub>O<sub>2</sub>, 1 $\mu$ M catalyst.

15

As with Example 1 above, the delta-R values are higher for those experiments in which more of staining is removed from the cloth. The results show that enhancers improve the performance of the catalyst under these conditions.

20

- 33 -

**Table 4: Delta-R Values for Tea Stained Cloth**

	Detergent liquor only	Detergent liquor plus peroxide	Detergent liquor plus peroxide and catalyst
Control (- enhancer)	4.3	4.6	4.9
'ECHA' (+ enhancer)	-	-	5.5
'ABTS' (+ enhancer)	-	-	5.7

5

**Example 5: Pick-up on white from Direct Green Dye:**

One 10x10cm Direct Green 26 dyed (unfixed) cotton cloth and one 10x10 cm white cotton monitor cloth were washed together  
 10 in a zeolite-built detergent liquor (1g/L 55/45 LAS/A7, 1.5g/L zeolite, 0.5g/L Na<sub>2</sub>CO<sub>3</sub>) 200ml liquor using a Rotawash (Linitester). Data values (delta E) shown in Table 5 are averages of 4 readings (2 per side, per monitor cloth).

15 In this experiment the delta-E represents the amount of dye which has been transferred from the green cloth to the white monitor. Therefore, lower levels of delta-E are representative of better results.

20 Where present, levels of additional components are: 100μM PTP, 1000μM H<sub>2</sub>O<sub>2</sub>, 1μM catalyst.

Results in Table 5 show that peroxide alone did nothing to prevent dye transfer. Addition of catalyst has an effect  
 25 which is further improved by the presence of the enhancer.

- 34 -

**Table 5: Delta-E values Direct Green Pick-up**

	Detergent liquor only	Detergent liquor plus peroxide	Detergent liquor plus peroxide and catalyst
Control (- enhancer)	22.6	22.5	11.5
'PTP' (+ enhancer)	-	-	7.7

- 35 -

**CLAIMS**

1. A composition comprising:

5

a) a non-enzyme, metal-complexing ligand which is capable, in its complexed form and in the presence of a source of oxidising equivalents, of oxidising dyestuffs and/or chromophoric soils, and,

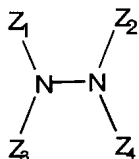
10

b) one or more enhancer compounds for the said metal complexing ligand.

2. Composition according to claim 1 wherein the enhancer compound is of the general formula shown below:

15

(general formula 1)



20

wherein:

a)  $Z_1$ - $Z_4$  are electron-withdrawing groups, independently selected from the group consisting of optionally substituted alkyl/(hetero) (poly)aryl-, -sulfone, -sulfoxide, -sulfonate, -carbonyl, -oxalyl, -amidoxalyl, -hydrazidoxalyl, -carboxyl and esters

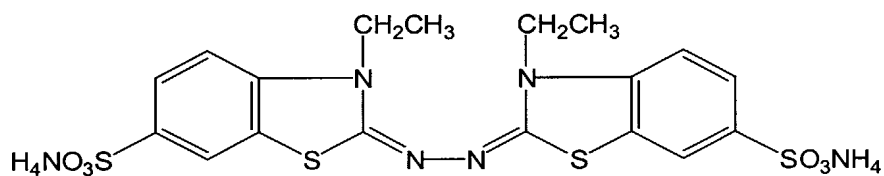
25

- 36 -

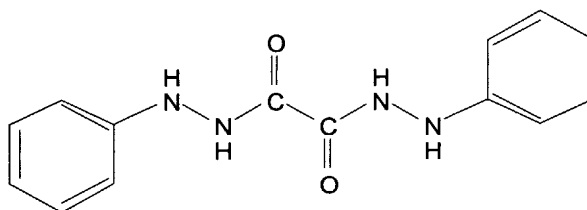
and salts thereof, -amidyl, -hydrazidyl, and nitrile, and,

b)  $Z_3$  and  $Z_4$  are hydrogen, or are absent when the bonding between  $Z_1$  or  $Z_2$  and the adjacent nitrogen in the general form is a pi-bond.

3) Composition according to claim 2 wherein the enhancer compound has the formula:

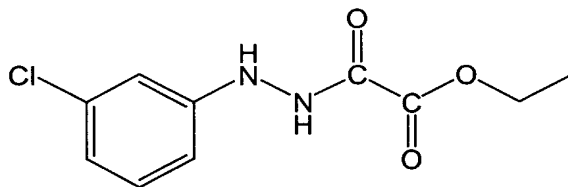


4) Composition according to claim 2 wherein the enhancer compound has the formula:

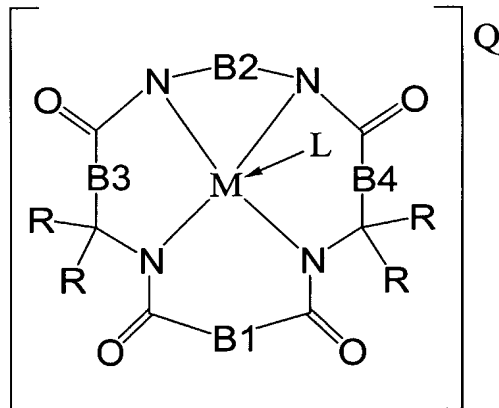


- 37 -

- 5) Composition according to claim 2 wherein the enhancer compound has the formula:



- 6) Composition according to any preceding claim wherein the metal-complexed ligands are those having the structure:



wherein:

- a)  $B_1$ ,  $B_3$  and  $B_4$  each represent a bridging group having zero, one two or three carbon containing nodes for substitution, and  $B_2$  represents a bridging group having at least one carbon containing node for

- 38 -

substitution, each said node containing a C(R),  
C(R<sub>1</sub>) (R<sub>2</sub>) or C(R)<sub>2</sub> ,

b) each R substituent is the same is the same or  
5 different from the remaining R substituents, and

1) is selected from the group consisting of  
alkyl, alkenyl, cycloalkyl, cycloalkenyl,  
aryl, alkynyl, alkylaryl, halogen, alkoxy,  
10 phenoxy and combinations thereof, or

2) forms a substituted or unsubstituted benzene  
ring of which two carbons on the ring form  
nodes in the B-unit;

15 c) M is a transition metal ion;

d) L is an axial ligand; and,

20 e) Q is an alkali metal counter-ion.

7. Composition according to any one of claims 1-6, further  
comprising a peroxygen source.

25 8. Composition according to claim 7, wherein the peroxygen  
source is hydrogen peroxide or a precursor thereof.

9. Composition according to any one of claims 1-8, further  
comprising surfactant and builder.



- 39 -

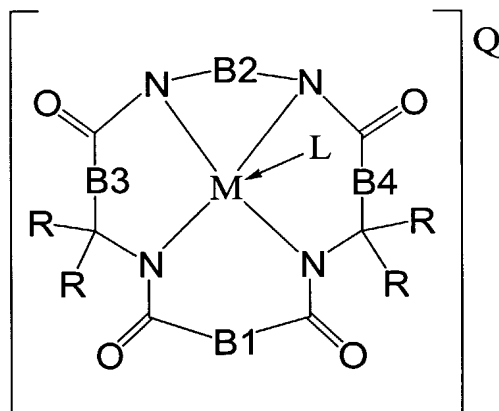
10. A laundry bleaching composition comprising:

a) at least one surfactant,

5

b) at least one builder,

c) a metal-complexed ligand having the structure:



10

wherein:

- 1)  $B_1$ ,  $B_3$  and  $B_4$  each represent a bridging group having zero, one two or three carbon containing nodes for substitution, and  $B_2$  represents a bridging group having at least one carbon containing node for substitution, each said node containing a  $C(R)$ ,  $C(R_1)(R_2)$  or  $C(R)_2$ ,

15

20

- 40 -

2) each R substituent is the same or different from the remaining R substituents, and

5 a) is selected from the group consisting of alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, phenoxy and combinations thereof, or

10 b) forms a substituted or unsubstituted benzene ring of which two carbons on the ring form nodes in the B-unit;

3) M is a transition metal ion;

15

4) L is an axial ligand; and,

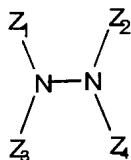
5) Q is an alkali metal counter-ion.

20 d) a peroxygen source, and,

e) one or more enhancer compounds for the said metal complexing ligand, at least one said enhancer compound being of the general formula shown below:

25

(general formula 1)



- 41 -

wherein:

- 1)  $Z_1$ - $Z_2$  are electron-withdrawing groups,  
independently selected from the group consisting  
of optionally substituted alkyl/(hetero)  
(poly)aryl-, -sulfone, -sulfoxide, -sulfonate, -  
carbonyl, -oxalyl, -amidoxalyl, -hydrazidoxalyl, -  
carboxyl and esters and salts thereof, -amidyl, -  
hydrazidyl, and nitrile, and,
- 2)  $Z_3$  and  $Z_4$  are hydrogen, or are absent when the  
bonding between  $Z_1$  or  $Z_2$  and the adjacent nitrogen  
in the general form is a pi-bond.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/08538

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/39 C11D3/32 C11D3/34

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 785 886 A (CHIN QUEE-SMITH CATHERINE VICT ET AL) 28 July 1998 (1998-07-28) column 2; claims; examples ---	1
X	US 5 474 576 A (FREDJ ADBENNACEUR ET AL) 12 December 1995 (1995-12-12) column 1; claims; examples ---	1
X	US 5 853 428 A (HORWITZ COLIN P ET AL) 29 December 1998 (1998-12-29) cited in the application column 12; claims; examples 33-39 ---	1,6-9
X	US 5 445 755 A (BUSCH ALFRED ET AL) 29 August 1995 (1995-08-29) cited in the application column 22; claims; examples --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

9 December 2002

Date of mailing of the international search report

23/12/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Pffannenstein, H

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/08538

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 12621 A (NOVO NORDISK) 9 June 1994 (1994-06-09) page 24 -page 26; claims; figures; examples ----	1-3
A	WO 95 31526 A (PROCTER & GAMBLE) 23 November 1995 (1995-11-23) page 1 -page 2; claims; examples ----	1-10
P,X	DE 102 00 672 A (KAO CORP) 11 July 2002 (2002-07-11) page 4; claims; examples -----	1,6-9

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 02/08538

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5785886	A	28-07-1998	US 5653910 A	05-08-1997
			AU 6002496 A	30-12-1996
			DE 69614224 D1	06-09-2001
			DE 69614224 T2	15-11-2001
			WO 9640855 A1	19-12-1996
			EP 0775192 A1	28-05-1997
			ES 2162066 T3	16-12-2001
			ZA 9604604 A	04-12-1997
US 5474576	A	12-12-1995	EP 0553608 A1	04-08-1993
			WO 9315176 A1	05-08-1993
			AU 4862693 A	07-07-1994
			CA 2127096 A1	05-08-1993
			CN 1075502 A	25-08-1993
			JP 7503278 T	06-04-1995
			MX 9300514 A1	29-07-1994
			TR 26405 A	15-03-1995
US 5853428	A	29-12-1998	US 5876625 A	02-03-1999
			AP 905 A	27-11-2000
			AU 720042 B2	25-05-2000
			AU 3735297 A	10-02-1998
			BR 9710514 A	24-10-2000
			CA 2261229 A1	29-01-1998
			CN 1230980 A	06-10-1999
			EP 0923635 A2	23-06-1999
			JP 2000515194 T	14-11-2000
			NO 990267 A	15-03-1999
			NZ 333795 A	28-07-2000
			PL 331352 A1	05-07-1999
			US 6136223 A	24-10-2000
			WO 9803626 A2	29-01-1998
			US 6241779 B1	05-06-2001
			AP 1013 A	27-09-2001
			AT 225844 T	15-10-2002
			AU 730906 B2	15-03-2001
			AU 3665597 A	10-02-1998
			BR 9710538 A	17-08-1999
			CA 2261228 A1	29-01-1998
			CN 1230979 A	06-10-1999
			DE 69716275 D1	14-11-2002
			EP 0918840 A1	02-06-1999
			JP 2001503073 T	06-03-2001
			NO 990266 A	22-03-1999
			NZ 333796 A	29-09-2000
			PL 331316 A1	05-07-1999
			WO 9803625 A1	29-01-1998
			US 6099586 A	08-08-2000
US 5445755	A	29-08-1995	EP 0763095 A1	19-03-1997
			JP 10501276 T	03-02-1998
			WO 9533042 A1	07-12-1995
WO 9412621	A	09-06-1994	BR 9307576 A	15-06-1999
			CA 2150562 A1	09-06-1994
			WO 9412621 A1	09-06-1994
			EP 0679183 A1	02-11-1995
			FI 952648 A	28-07-1995

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 02/08538

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9412621	A		JP 8506009 T	02-07-1996
			US 5965510 A	12-10-1999
			AU 7937194 A	22-05-1995
			CA 2175047 A1	04-05-1995
			WO 9511964 A1	04-05-1995
			EP 0730641 A1	11-09-1996
			US 5948661 A	07-09-1999
			BR 9307575 A	15-06-1999
			CA 2150563 A1	09-06-1994
			WO 9412620 A1	09-06-1994
			EP 0677102 A1	18-10-1995
			FI 952647 A	31-05-1995
			JP 8503371 T	16-04-1996
-----				
WO 9531526	A	23-11-1995	CA 2189747 A1	23-11-1995
			CN 1151756 A	11-06-1997
			EP 0759968 A1	05-03-1997
			JP 10500167 T	06-01-1998
			WO 9531526 A1	23-11-1995
			US 5908821 A	01-06-1999
-----				
DE 10200672	A	11-07-2002	DE 10200672 A1	11-07-2002
			JP 2002275499 A	25-09-2002
			US 2002134965 A1	26-09-2002
-----				